Non-linear thermoelectricity and cooling effects in metallic constrictions

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Non-linear thermoelectricity and cooling effects in metallic constrictions

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Abstract. Linear as well as non-linear contributions to the Zeebeck and Peltier coefficients of a metallic film in contact with the equilibrium metal are calculated within a simple model. The non-linear part of the thermoelectric response survives down to a very low temperature which in principle permits thermoelectric cooling at these conditions. Thermal equilibrium in a metallic constriction between dissimilar metals is evaluated in the non-linear current-carrying regime.

1. Introduction

Small metallic and semiconducting specimens develop a number of specific low-temperature phenomena including flux quantization and persistent currents in normal-metal loops [1], charge discreteness effects in tiny metallic granules [2, 3], non-equilibrium electron–phonon states in metallic microconstrictions (point contacts [4, 5]), etc. Mostly these phenomena, which are promising for novel microelectronic applications, are displayed at quite a low temperature. In these conditions, the electron and phonon systems of a metal can be easily driven out of equilibrium, which changes the state of the kinetic processes. Some questions which have been the subject of controversy for years can be subjected to theoretical investigation and experimental tests, for example why the resistivity is non-zero when phonons are dragged after electrons (the Peierls problem), or how the Joule heating takes place when scattering of electrons is purely elastic. (The Drude formula gives a finite resistivity at $l_i = \infty$.)

We shall partly answer the last question by considering the limit of large but finite inelastic electron mean free path l_i. The conductivity is not much affected by inelastic scattering processes whereas thermoelectric coefficients are, provided that the current is not small. In the non-linear regime, thermoelectric coefficients are strongly enhanced at large l_i. The possibility of using this effect for thermoelectric cooling at very low temperatures will be discussed in section 4.

2. Formulation of the model

We consider a degenerate electron gas interacting elastically with impurities (or other defects of the crystalline lattice) and inelastically with phonons, electrons, etc. Inelastic relaxation

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provided by electron–phonon interaction becomes ineffective at low temperatures and low excitation energies with the corresponding scattering rate

$$\tau_i^{-1} \simeq (T^3 + \varepsilon^3)/\Theta_D^2 \tag{1}$$

where Θ_D is the Debye temperature and ε the energy of electron relative to the Fermi energy.

We suppose that electrons in a metal film M (figure 1) can tunnel to a bulk metal M′, the latter being considered as a thermostat for M. The interaction between M and M′ is described by a tunnelling Hamiltonian

$$H_T = W \sum_{p,q} (a_p^+ b_q + b_q^+ a_p) \tag{2}$$

where $a_p^+(a_p)$ creates (annihilates) an electron in M whereas $b_q^+(b_q)$ does the same in M′.

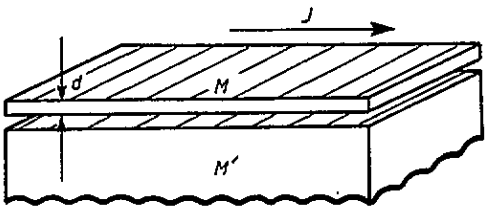

Figure 1. Schematic diagram of a tunnelling junction between a metal film and a bulk metal. J is the current passing through the film.

Calculating perturbatively the occupation $f_p = \langle a_p^+ a_p \rangle$ change due to (2), one obtains

$$\left(\frac{df_p}{dt}\right)_{coll} = -2\pi W^2 \sum_q (f_p - f_q)\delta(\varepsilon_p - \varepsilon_q). \tag{3}$$

If we assume that electrons in metal M′ relax to their equilibrium by some inelastic mechanism different from (2) and stronger than the latter, such that we may consider f_q to be the equilibrium distribution, then (3) becomes the collision integral

$$I_i = -\frac{1}{\tau_i}(f_p - f_p^0) \tag{4}$$

with

$$\tau_i^{-1} = 2\pi W^2 N(0) \tag{5}$$

and

$$f_p^0 = \frac{1}{\exp(\varepsilon_p/T) + 1} \qquad \xi_p = \varepsilon_p - \mu. \tag{6}$$

T is the equilibrium temperature of M′. The inelastic relaxation time τ_i can be related to the tunnelling resistance between M and M′ according to

$$R_N^{-1} = e^2 N(0) \frac{Sd}{\tau_i} \tag{7}$$

where $N(0)$ is the density of electronic states at the Fermi energy, and S and d are the surface area and the thickness of a film, respectively.

Elastic scattering can be written as (e.g. see [6])

$$I_e = -\sum_{p'} W_{pp'}(f_p - f_{p'})\delta(\varepsilon_p - \varepsilon_{p'}) \tag{8}$$

where $W_{pp'}$ is the electron–impurity scattering amplitude.

The purpose of this term is to redistribute electrons over the Fermi surface once they are driven out of equilibrium by the electric field. We shall simplify equation (8) to the form

$$I_e = -\frac{f_p - f_{-p}}{2\tau_e} \tag{9}$$

thus providing for the scattering $p \to -p$ only. This is enough to establish the time-independent electron distribution in the current-carrying state. We do not think that selection of the simplified electron–impurity scattering may change qualitatively the conclusions concerning the non-equilibrium current-carrying state to be discussed in the next section.

The kinetic equation for the electronic distribution function is

$$\frac{\partial f_p}{\partial t} + v \cdot \frac{\partial f_p}{\partial r} + eE \cdot \frac{\partial f_p}{\partial p} = I_i + I_e. \tag{10}$$

Inelastic scattering (4) does not ensure automatically charge neutrality (as for example the electron–phonon scattering does) in the continuity equation following from (10):

$$\frac{\partial n}{\partial t} + \operatorname{div} j + \frac{1}{\tau_i}\sum_p (f_p - f_p^0) = 0. \tag{11}$$

This can be improved if we suppose that, instead of (4),

$$I_i = -\frac{1}{\tau_i}[f_p - f_p^0(\mu')] \tag{12}$$

where μ' is the renormalized chemical potential derived self-consistently from the charge neutrality condition

$$\sum_p f_p = n_0 = \sum_p f_p^0. \tag{13}$$

The shift in μ appears because of the voltage between M and M'. In the homogeneous time-independent state, equation (13) is always satisfied with the unperturbed chemical potential μ owing to the condition (11).

Conventional scattering theory [6] based on the linear-response expansion

$$f_p = f_p^0 + f_p^1 \tag{14}$$

with $f_p^1 \sim E$ has a puzzling feature that the current j remains finite at $I_i = 0$. However, if we try to take into account the next terms in (14) proportional to E^2, E^3, etc, we find

that non-linear corrections are divergent. Therefore, the non-perturbative solution of the Boltzmann equation is required. This can be achieved within the model adapted

$$\frac{\partial f}{\partial t} + v \cdot \frac{\partial f}{\partial r} + eE \cdot \frac{\partial f}{\partial p} = -\frac{f_p - f_{-p}}{2\tau_e} - \frac{f_p - f_p^0(\mu')}{2\tau_i} \tag{15}$$

and

$$\sum_p (f_p - f_p^0) = 0. \tag{16}$$

A similar model has been considered by Sarker *et al* [7] who introduced, in the elastic collision term, an unknown (isotropic) distribution function to be determined self-consistently. These workers, in their study of the non-linear conduction regime, have not considered thermoelectric effects.

Choose f_p in the form

$$f_p = f_p^0 + F_p + G_p \tag{17}$$

where F_p is an even and G_p an odd function of p, and calculate the electric current density j and the heat current density q according to [8]

$$j = 2e \int d\tau_p \, v G_p \qquad q = 2 \int d\tau_p \, v \xi_p G_p \tag{18}$$

where the factor 2 is due to spin degeneracy and $d\tau_p = dp/(2\pi)^3$. Solution of the kinetic equation at $T = 0$ gives

$$G_p = \frac{\tau e}{m} \int dr \frac{\exp(ip \cdot r)}{1 + \tau \tau_i e^2 (E \cdot r)^2} \int d\tau_{p'} \, (E \cdot p') \delta(\xi_{p'}) \exp(-ip' \cdot r) \tag{19}$$

and

$$F_p = -\tau_i e E \cdot \frac{\partial}{\partial p} G_p \tag{20}$$

where τ is the relaxation time given by

$$\tau^{-1} = \tau_e^{-1} + \tau_i^{-1}. \tag{21}$$

Simple calculation gives $j = (ne^2\tau/m)E$, whereas for the electron distribution function we obtain

$$G_p = \frac{1}{2}\sqrt{\frac{\tau}{\tau_i}} \exp\left(-\frac{|\xi_p|}{eE\sqrt{\tau\tau_i}|v_z|}\right) \operatorname{sgn}(v_z) \tag{22}$$

and

$$F_p = \tfrac{1}{2} \exp\left(-\frac{|\xi_p|}{eE\sqrt{\tau\tau_i}|v_z|}\right). \tag{23}$$

Therefore, the Drude formula is exact at $\tau_i \to \infty$ whereas the distribution of electrons is strongly different from the conventional linear-response drift state.

Note that F_p is not small at $\xi_p = 0$ even at $\tau_i \to \infty$. The electron distribution is narrowed in the energy interval

$$\delta E \simeq eE\sqrt{l l_i} \qquad l = v_F \tau \tag{24}$$

which can be considered as an effective electronic temperature T^* of the current-carrying state.

3. Non-linear transport coefficients

Suppose that an electric field $\boldsymbol{E}$ and a temperature gradient ∇T exist in a metal. Transport equations for the even and odd parts of the distribution function (17) read, according to (15),

$$\left(v \cdot \frac{\partial}{\partial r} + e\boldsymbol{E} \cdot \frac{\partial}{\partial \boldsymbol{p}}\right) G_p + \frac{1}{\tau_i} F_p = 0 \tag{25}$$

and

$$\left(v \cdot \frac{\partial}{\partial r} + e\boldsymbol{E} \cdot \frac{\partial}{\partial \boldsymbol{p}}\right) F_p + \frac{1}{\tau} G_p = \left(\frac{\xi_p}{T} \nabla T - e\boldsymbol{E}\right) \cdot v \frac{\partial f_p^0}{\partial \xi_p}. \tag{26}$$

If $\boldsymbol{E}$ and ∇T are space and time independent, G_p is determined from the second-order differential equation

$$\left(1 + \tau \tau_i e^2 E_i E_j \frac{\partial^2}{\partial p_i \partial p_j}\right) G_p = \tau \left(\frac{\xi_p}{T} \nabla T - e\boldsymbol{E}\right) \cdot v \frac{\partial f_p^0}{\partial \xi_p}. \tag{27}$$

The solution to equation (27) is achieved through the Fourier transformation

$$G(\boldsymbol{R}) = \int \mathrm{d}\tau_p \, G_p \exp(\mathrm{i}\boldsymbol{p} \cdot \boldsymbol{R}) \tag{28}$$

which gives

$$G_p = \tau \int \mathrm{d}r \frac{\exp(\mathrm{i}\boldsymbol{p} \cdot r)}{1 + \tau \tau_i e^2 (\boldsymbol{E} \cdot r)^2} \int \mathrm{d}\tau_{p'} \left(\frac{\xi_{p'}}{T} \nabla T - e\boldsymbol{E}\right) \cdot v' \frac{\partial f_{p'}^0}{\partial \xi_{p'}} \exp(-\mathrm{i}\boldsymbol{p}' \cdot r) \tag{29}$$

and

$$F_p = -\tau_i e\boldsymbol{E} \cdot \frac{\partial}{\partial \boldsymbol{p}} G_p. \tag{30}$$

Substituting equation (29) into equation (18) and performing an integration over the momentum p, one obtains

$$j = \frac{2\mathrm{i}e\tau}{m} \int \mathrm{d}\tau_p \left(\frac{\xi_p}{T} \nabla T - e\boldsymbol{E}\right) \cdot v \frac{\partial f_p^0}{\partial \xi_p} \frac{\partial}{\partial r} \left(\frac{\exp(-\mathrm{i}\boldsymbol{p} \cdot r)}{1 + \tau \tau_i e^2 (\boldsymbol{E} \cdot r)^2}\right)_{r=0} \tag{31}$$

and

$$q = -\frac{2\mathrm{i}\tau}{m} \int \mathrm{d}\tau_p \left(\frac{\xi_p}{T} \nabla T - e\boldsymbol{E}\right) \cdot v \frac{\partial f_p^0}{\partial \xi_p} \frac{\partial}{\partial r} \left[\left(\frac{1}{2m} \frac{\partial^2}{\partial r^2} + \mu\right) \left(\frac{\exp(-\mathrm{i}\boldsymbol{p} \cdot r)}{1 + \tau \tau_i e^2 (\boldsymbol{E} \cdot r)^2}\right)\right]_{r=0}. \tag{32}$$

The non-linear term does not appear in equation (31) after taking the limit $r \to \mathbf{0}$, and we obtain for j

$$j = \frac{ne^2\tau}{m} \boldsymbol{E} - \frac{\pi^2 ne\tau}{p_F^2} T \nabla T. \tag{33}$$

Therefore, the conductivity is expressed by the conventional Drude formula, at least for the simplified collision integral in the form of equations (4) and (9). The second point is that the weak inelastic scattering does not change the current density and the conductivity of a metal appreciably.

However, the heat conductivity is strongly affected by inelastic scattering and acquires non-linear contributions in E and ∇T. Evaluation of equation (32) results in

$$q = \frac{\pi^2 ne\tau}{p_F^2} T^2 E - \frac{\pi^2 n\tau}{3m} T\nabla T + q' \tag{34}$$

where

$$q' = -\frac{\pi^2 ne^2\tau^2\tau_i}{m^2}\left(\frac{T}{\mu}[|E|^2\nabla T + 2(E\cdot\nabla T)E] - 3|E|^2 eE\right). \tag{35}$$

The linear part of the kinetic coefficients satisfies the Onsager reciprocity relation $T\partial j/\partial(\nabla T) = -\partial q/\partial E$ [6].

According to the above expression, the Peltier coefficient Π is determined as

$$\Pi = \left(\frac{\partial q}{\partial j}\right)_{\nabla T=0} = \frac{\pi^2 T^2}{2e\mu} + \frac{3\pi^2 e\tau\tau_i}{m}|E|^2. \tag{36}$$

Comparing this with equation (24) we see that the second contribution resembles a contribution due to an effective temperature T^* proportional to the electric field: $T^* \propto eE\sqrt{ll_i}$. At low ambient temperatures, this contribution becomes dominant.

4. Is non-linear thermoelectric cooling possible?

The main reason for failure of thermoelectric cooling at low temperatures is the fast disappearance of the linear Peltier coefficient Π as $T \to 0$. The phonon drag increase in Π [9] does not help much as it also disappears at low temperatures. (However, in small resistors, electron–phonon interaction may result in the important phonon-drag contribution [10].) The question arises naturally of whether the non-linear temperature-independent part of Π (equation (36)) may help. As we increase E, the Joule heating increases, thus reducing the effect of thermoelectric cooling. Let us estimate whether this is always the case.

Consider a thermoelectric circuit between two metallic films with different inelastic mean free times τ_i and equal elastic mean free times τ_e. (We assume that $\tau_i \gg \tau_e$; therefore the total relaxation time τ is the same in both films.) This can be done by changing the thickness of a tunnelling barrier between a film and the bulk metal slightly, thus providing for the corresponding change in τ_i. Parts of the film with different barrier transmissivities can be considered as different metals A and B in the thermoelectric circuit in figure 2, resulting in a heat release (or absorption, depending on the direction of the current) at the point of connection according to

$$Q_{\text{Peltier}} = (\Pi_A - \Pi_B)j. \tag{37}$$

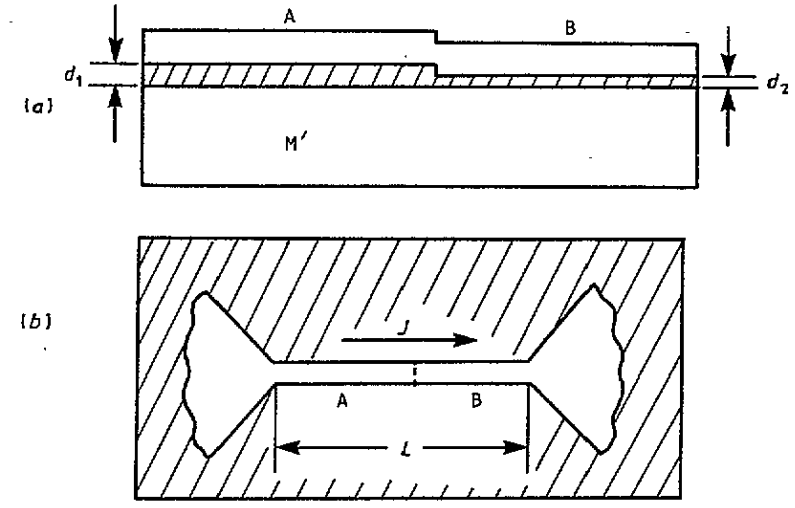

Figure 2. (a) Cross section and (b) in-plane view of a thermoelectric constriction.

This heat is released within the characteristic length of the order of $\sqrt{ll_i}$. The Joule heat at the same region will be

$$Q_{\text{Joule}} \simeq \frac{ne^2\tau}{m} E^2 \sqrt{ll_i}. \tag{38}$$

An estimate of the ratio $Q_{\text{Peltier}}/Q_{\text{Joule}}$ on the assumption that $|\Pi_a - \Pi_b| \simeq \Pi$ gives according to (36)

$$\frac{Q_{\text{Peltier}}}{Q_{\text{Joule}}} \sim \frac{eE\lambda}{\mu} \qquad \text{at } T^* \gg T. \tag{39}$$

This may in principle be larger than unity at very strong electric fields. If we assume that the constriction length L in figure 2 is larger than the energy relaxation length $\lambda = \sqrt{ll_i}$, then this means practically that the bias at the microconstriction should be greater than the Fermi energy. This corresponds to an electron drift velocity of the order of

$$v_d \sim v_F(l/l_i)^{1/2} \tag{40}$$

which is still much smaller than the Fermi velocity.

Let us make some numerical estimates. For a tunnelling junction of size 1 mm × 1 mm and film thickness $d \simeq 10^{-6}$ cm, one obtains, according to (7), $\tau_i \simeq 10^{-10}$ s at $R_N \simeq 10^{-6}\ \Omega$. With the realistic assumption $l \simeq 10^{-6}$ cm, this gives $\lambda \simeq 10^{-4}$ cm. Therefore, very-high-transmissivity junctions are required to obtain reasonable values of λ, and therefore of the contact length. The possibility of thermoelectric cooling in a device of the type shown in figure 2 appears to be questionable; however, it is not completely ruled out.

If the constriction size is smaller than λ, the right-hand side of (40) will acquire an extra factor L/λ because the Joule heat is then released mainly at the banks of the constriction where it produces a negligible effect. However, our formula (36) does not apply directly to this 'diffusive' regime of the constriction current-carrying state (according to the definition in [4]). For small drift velocities $v < v_F(l/l_i)^{1/2}\lambda/L$, the thermoelectric effect will manifest itself in the asymmetry of the current–voltage characteristic of the contact [10].

The experimental situation in studying non-linear transport in metals is not clear. Electron heating in the strong-current regime has been observed in metal films [11, 12] and metallic microbridges [13]. However, thermoelectric effects have not been detected. In very narrow metallic constrictions (point contacts), the thermoelectricity shows up in the dependence of resistance on the direction of the current [14–16].

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